



**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re application of  
Makoto FUNABASHI    Attorney Docket No. 1982-0153P  
Appln. No.: 09/612,543  
Confirmation No.: 9387    Group Art Unit: 1762  
Filed: July 7, 2000    Examiner: Michael B. CLEVELAND  
For:           **METHOD FOR MANUFACTURING RADIATION IMAGE  
CONVERSION PANEL**

***DECLARATION UNDER 37 C.F.R. § 1.132***

Commissioner for Patents  
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Sir:

I, Masaharu NAKATSU, hereby declare and state:  
THAT I am a citizen of Japan;  
THAT I graduated from Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology in March, 1991, and my major was Material Science;  
THAT I joined Fuji Photo Film Co., Ltd., in April, 1991, and since then until June, 2000 I have been working at Ashigara Research Laboratory of the company and have been engaged in research for photographic photosensitive materials, and since June, 2000 until present I have been working at Miyanodai Technology Development Center of the company and have been engaged in research for phosphor;  
THAT I am familiar with the prosecution of the above-identified application; and  
THAT the experimentation set forth below was conducted by me or under my direct supervision.

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## EXPERIMENT

### EXAMPLE 1

In order to verify the effects of differences between coating liquid preparation processes on the image quality characteristics of a radiation image conversion panel, the following experiment was conducted.

A mixture of raw materials was prepared in the same manner as described in "1: Manufacturing of calcined product" in EXAMPLE 1 of the present invention.

First, by thoroughly mixing the raw materials as described in the following composition of raw materials, a mixture of raw materials was prepared. The mixture of these raw materials was not subjected to calcination.

#### **<Composition of raw materials>**

BaFBr:Eu (Eu concentration is  $5.0 \times 10^{-3}$  in molar ratio, and average grain diameter is  $6.5 \mu\text{m}$ )  $\cdots$  12,480 g

BaFI:Eu (Eu concentration is  $5.0 \times 10^{-3}$  in molar ratio, and average grain diameter is  $7.1 \mu\text{m}$ )  $\cdots$  2,640 g

BaF<sub>2</sub> ... 248 g

The mixture was divided into four equal parts (raw material A, raw material B, raw material C, and raw material D), and raw material A and raw material C were calcined under the following conditions to prepare calcined product A and calcined product C.

### (Calcining process)

Each raw material was charged into a calcining container (quartz glass boat, 30 cm long, 15 cm wide, and 5 mm thick). The calcining containers were placed in the calcining space of an electric furnace (a tube furnace with a calcining space of 100 liters) which furnace

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atmosphere temperature was set at 850 °C, and kept heated in a nitrogen gas atmosphere for 2 hr. Thereafter, the calcining space was changed into a slightly oxidizing atmosphere containing 1.3% oxygen, and the heating was continued for another 1 hr. Then, the calcining containers were moved into the cooling space, where they were cooled down to 200 °C or below while being kept isolated from the atmosphere, and the calcined product were taken out into the atmosphere.

For each of the calcined product A and raw material B, coating liquid A and coating liquid B were prepared through the following processes:

(Aggregate reduction process)

1.5 kg of the calcined product obtained above was placed in 2 liters of methylethylketone (MEK) contained in a 4-liter beaker, and the mixture was stirred at 200 rpm for 15 hr, using a propeller stirrer (Three-One Motor, HEIDON BL1200, manufactured by Shinto Scientific Co., Ltd.), in the aggregate reduction processing, thereby obtaining a slurry.

(Wet classification process)

The slurry obtained by the aggregate reduction process was wet-classified with a screen covered with a 20-µm nylon mesh.

(Phosphor density adjustment process)

The wet-classified slurry was placed in a 4-liter beaker, and allowed to stand for 30 min. By discarding the supernatant (by decantation), the density of the stimulable phosphor in the slurry was adjusted to 80 wt %. This density was defined as the theoretical one which is based on the subtraction of the weight, k (kg), of the stimulable phosphor given as the classification residue after the wet classification process from the total weight (1.5 kg) of the calcined product charged into the aggregate reduction process. Specifically, the value of density can be determined from the following formula. In the formula, V denotes the weight (kg) of the concentrated dispersion medium (MEK to provide the solvent later).

$$\text{Phosphor density (wt \%)} = (1.5 - k) / [(1.5 - k) + V] \times 100$$

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(Coating liquid preparation process)

By adding 30.0 g of polyurethane (PANDEX T-5265H, manufactured by Dainippon Ink and Chemicals, Inc.), 7.8 g of epoxy resin (EP1001 [solid], manufactured by Yuka-Shell Epoxy Co., Ltd.), and 2.3 g of polyisocyanate (CORONATE HX, manufactured by Nippon Polyurethane Industry Co. Ltd.) to 1.0 kg of the concentrated slurry obtained by the above-described phosphor density adjustment process, and dispersing them with a propeller mixer to prepare a coating liquid with a viscosity of 40 PS.

By mixing each of calcined product C and raw material D with methylethylketone (MEK) to a density of 80 wt %, and stirring the respective mixtures at 200 rpm for 15 hr in a 4-liter beaker, using a propeller stirrer (Three-One Motor, HEIDON BL1200, manufactured by Shinto Scientific Co., Ltd.) for reducing aggregate to obtain slurry C and slurry D.

To 1.0 kg of each of the slurry C and slurry D obtained, 30.0 g of polyurethane (PANDEX T-5265H, manufactured by Dainippon Ink and Chemicals, Inc.), 7.8 g of epoxy resin (EP1001 [solid], manufactured by Yuka-Shell Epoxy Co., Ltd.), and 2.3 g of polyisocyanate (CORONATE HX, manufactured by Nippon Polyurethane Industry Co. Ltd.) were added and dispersed with a propeller mixer in the same manner as in the above-described coating liquid preparation process to prepare blended liquid C and blended liquid D.

By wet-classifying the prepared blended liquid C and blended liquid D, respectively, with a vibrating screen covered with a 20- $\mu$ m nylon mesh in the same manner as in the above-described wet classification process to prepare coating liquid C and coating liquid D.

By using the phosphor layer coating liquids A to D obtained, radiation image conversion panels A to D were manufactured in the following manner:

(Phosphor layer forming process)

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(1) Preparation of phosphor sheet

By applying each of the phosphor layer coating liquids obtained above to a temporary support made of polyethylene terephthalate (180  $\mu\text{m}$  thick) coated with a silicone release agent, drying it, and then peeling it off from the temporary support, a phosphor sheet (320  $\mu\text{m}$  thick) was prepared.

(2) Formation of reflective (undercoating) layer

<Composition of reflective layer>

- Fine grains of gadolinium oxide ( $\text{Gd}_2\text{O}_3$ ) (90 wt % of all of which have grain size in the range of 1 to 5  $\mu\text{m}$ ) 30 parts
- Binding agent: Soft acrylic resin (CRISCOAT P-1018GS (20% solution), manufactured by Dainippon Ink and Chemicals Inc.) 30 parts
- Phthalate ester 3.5 parts
- Electrically conducting material: ZnO whiskers 10 parts
- Coloring agent: Ultramarine blue 0.4 parts

By adding the proper quantity of MEK (methylethylketone) to the materials of the above-mentioned composition, and dispersing and mixing them using a dissolver, a reflective (undercoat) layer formation coating liquid with a viscosity of 10 PS (20 °C) was prepared. By horizontally placing a support made of polyethylene terephthalate with a thickness of 300  $\mu\text{m}$  on a glass plate, uniformly applying the above-mentioned undercoat layer formation coating liquid to the surface of the support, using a doctor blade, and then drying the coated film, a reflective layer (20  $\mu\text{m}$  thick) was formed on the surface of the support.

(3) Formation of phosphor layer

The previously prepared phosphor sheet was placed on the reflective layer formed on the surface of the support for carrying out thermocompression bonding. The thermocompression bonding operation was continuously performed, using calendar rolls, under a pressure of 500 kgw/cm<sup>2</sup>, at a temperature of 90 °C for the upper roll, a temperature of 75 °C for the lower roll, and a feed rate of 1.0 m/min. By this thermocompression bonding, the reflective layer formed on the

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surface of the support and the phosphor sheet were completely fused with each other, resulting in a phosphor layer being formed. The thickness of the phosphor layer after being fused was 220  $\mu\text{m}$ .

(Formation of protective film)

<Composition of protective film>

- Fluoroolefin: Fluoroolefin vinyl ether copolymer (LUMIFLON LF-504X (40% solution), manufactured by Asahi Glass Co., Ltd.) 50 parts
- Crosslinking agent: Polyisocyanate (OLESTER NP38-70S (70% solution), manufactured by Mitsui Toatsu Chemicals, Inc.) 9 parts
- Lubricant: Alcohol-modified silicone (X-22-2809 (66% solution), manufactured by Shin-Etsu Chemical Co., Ltd.) 0.5 parts
- Catalyst: Dibutyltine dilaurate (KS1260, manufactured by Kyodo Chemical Co., Ltd.) 3 parts

By dissolving the materials of the above-mentioned composition in the proper quantity of methylethylketone/cyclohexane (2/8 in volume ratio), a protective film formation coating liquid with a viscosity of 0.3 PS was prepared. By applying the protective film formation coating liquid to the above-mentioned phosphor layer with a doctor blade, and thermally curing and drying it by subjecting it to a heat treatment at 120 °C for 30 min, a protective film with a thickness of 3  $\mu\text{m}$  was formed.

In this way, radiation image conversion panels A to D each consisting of a support, an undercoat layer, a phosphor layer, and a protective film were prepared.

First, the amount of stimulable emission was determined by the following method.

Each of the radiation image conversion panels A to D obtained was punched to create a 10-mm-dia test piece, which was set in a cylindrical holder (with a recess opening 10 mm dia by 1 mm deep). In a dark room, the surface of the phosphor in the holder recess opening was irradiated with an X-ray beam of a tube voltage of 80 kVp at 100 mR, through an Al filter 3 mm thick, using an X-ray generator (MG164, manufactured by

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Philips Electronics N.V.). Twenty seconds thereafter, the surface of the phosphor was irradiated with a uniformly spread beam from a semiconductor laser diode (ML-1016R, manufactured by Mitsubishi Electric Corporation), having a wavelength of 660 nm, at an excitation energy of  $4.3 \text{ J/m}^2$ . At that time, the energy of the stimulable emission radiated from the surface of the phosphor was received by a photomultiplier tube (R-1848, manufactured by Hamamatsu Photonics K.K.), through an optical filter (B-410, manufactured by Hoya Corporation), to determine the amount of stimulable emission.

The measurements were expressed as relative values, assuming that the value of radiation image conversion panel A is 100.

From the measurement results, it was revealed that radiation image conversion panels B and D (both were comparative examples), which were manufactured using uncalcined product, hardly exhibited stimulable emission, and their image qualities were so poor to be not worthy of evaluation.

Next, the graininess of radiation image conversion panels A and C, which exhibited stimulable emission, was evaluated by the following method.

The radiation image conversion panels were irradiated with X-ray at a tube voltage of 80 kVp, and then scanned with a He-Ne laser beam (632.8 nm) to excite the phosphor. The stimulable emission radiated from the phosphor layer was received to be converted into an electric signal, which was then reproduced as an image on a display device, using an image reproducing device. The sharpness of the image obtained was determined with the modulation transfer function (MTF) (modulation frequency: 2 cycles/mm), and the graininess (RMS) at a dose of 0.1 mR was determined. The results are given in Table 1.

From the measurement results, it was found that the graininess of radiation image conversion panel A (the present invention), with which the calcined product was wet-classified before being mixed with the binder, was excellent and about 40% better than that of radiation image

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conversion panel C (comparative example), with which the calcined product was mixed with the binder before being wet-classified.

It is apparent from Table 1 that the unexpected results are obtained by selecting order of performing process steps.

Table 1

Radiation image conversion panel	Coating liquid preparation process	Sensitivity	Graininess ( $\times 10^{-3}$ )	Remarks
A	Calcined product was wet-classified before being mixed with binder	100	3.2	Present invention
B	Uncalcined product was wet-classified before being mixed with binder	0.13	—	Comparative example
C	Calcined product was mixed with binder before being wet-classified	91	5.3	Comparative example
D	Uncalcined product was mixed with binder before being wet-classified	< 0.1	—	Comparative example

EXAMPLE 2

In order to verify the effects of vigorous stirring in a large quantity of dispersion medium and ball milling on the samples, the following experiment was conducted.

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Raw materials E and F, which were the same as the raw material A as mentioned in EXAMPLE 1, and calcined product G and H, which were the same as the calcined product A, were prepared.

100 g of each of raw material E and calcined product G was added to 425 ml of an ethanol-water mixture (ethanol/H<sub>2</sub>O volume ratio = 80/20, containing lauric acid at 0.01 mol/l) prepared in a 1-liter stirring tank, and vigorously stirred at 500 rpm for 2 hr, using a propeller stirrer (Three-One Motor, HEIDON BL1200, manufactured by Shinto Kagaku Co., Ltd.).

Each powder was allowed to stand, and the supernatant was eliminated. By redispersing each powder in 425 ml of ethanol, allowing the mixture to stand, eliminating the supernatant, and drying the remainder at 60 °C, samples E and G were obtained.

For raw material F and calcined product H, mixture F and mixture H were prepared, respectively, in accordance with the following mixture composition.

### < Mixture composition >

Polyurethane (PANDEX T-5265H, manufactured by Dainippon Ink and Chemicals, Inc.) ⋯ 4.13 wt%

Epoxy resin (EP1001 [solid], manufactured by Yuka-Shell Epoxy Co., Ltd.) ··· 1.07 wt%

Polyisocyanate (CORONATE HX, manufactured by Nippon Polyurethane Industry Co. Ltd.) 32 wt%

Each of the mixtures F and H was ball-milled for 16 hr, using a ball mill (UNIVERSAL BALL MILL MODEL UB-31, manufactured by Yamato Scientific Co., Ltd.). Thereafter, the mixtures were filtered with a 200-mesh screen, and dried to obtain samples F and H.

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The amount of stimulable emission was measured by the following method.

For each of samples E, F, G and H, 200 mg of sample powder was uniformly charged into a black cylindrical holder (with a recess opening 10 mm dia by 1 mm deep). In a dark room, the surface of the phosphor in the holder recess opening was irradiated with an X-ray beam of a tube voltage of 80 kVp at 100 mR, through an Al filter 3 mm thick, using an X-ray generator (MG164, manufactured by Philips Electronics N.V.). Twenty seconds thereafter, the surface of the phosphor was irradiated with a uniformly spread beam from a semiconductor laser diode (ML-1016R, manufactured by Mitsubishi Electric Corporation), having a wavelength of 660 nm, at an excitation energy of 4.3 J/m<sup>2</sup>. At that time, the energy of the stimulable emission radiated from the surface of the phosphor was received by a photomultiplier tube (R-1848, manufactured by Hamamatsu Photonics K.K.), through an optical filter (B-410, manufactured by Hoya Corporation), to determine the amount of stimulable emission.

The measurements were expressed as relative values, assuming that the value of sample G is 100, and the results are given in Table 2.

Table 2

Sample name	Calcined or uncalcined	Process applied to samples	Amount of stimulable emission	Remarks
E	Uncalcined	Stirring	0.1	Comparative example
F	Uncalcined	Ball milling	< 0.1	Comparative example
G	Calcined	Stirring	100	Present invention
H	Calcined	Ball milling	47	Comparative example

Comparison between sample E and sample G, or between sample F and

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sample H, illustrates that the samples not subjected to calcination exhibited an insufficient amount of stimulable emission. Moreover, comparison between sample H which was ball-milled, and sample G which was vigorously stirred at 500 rpm, shows that ball milling remarkably decreases the amount of stimulable emission.

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: March 31, 2005

Masaharu Nakatsu  
Masaharu NAKATSU